HIGH PRESSURE PD-METAL/SILICATE PARTITION COEFFICIENTS: CONFIRMATION OF THE LATE VENEER HYPOTHESIS A.Holzheid[1], P.Sylvester[2], H.Palme[1], H.St.C.O'Neill[2], D.C.Rubie[3], [1]Universität zu Köln, Institut für Mineralogie und Geochemie, Zülpicherstr. 49b, 50674 Köln, Germany, [2] Australian National University, Canberra, Australia, [3] Bayerisches Geoinstitut, Bayreuth, Germany.

It has been known for a long time that the abundances of siderophile elements in the upper mantle of the Earth are higher than predicted by equilibration of core forming metal with mantle silicates using low pressure and temperature metal/silicate partition coefficients.

This excess is particularly dramatic for the highly siderophile elements (HSE) Ir, Re, Os, Ru, Pt, Rh, Pd and Au. Recently several authors claimed (e.g., [1],[2]) that, at high temperatures and/or high pressures the metal/silicate partition coefficients are much lower allowing equilibrium distribution between core and mantle. We have experimentally determined the Pd-metal/silicate partition coefficients at pressures from 1 to 20 GPa (ca. 600 km depth) and we find no decrease of the partition coefficients with pressure. Together with earlier results on the temperature dependence of the Pd-metal/silicate partition coefficients [3] the new data show that the abundances of the highly siderophile elements in the upper mantle cannot be established by equilibrium distribution between core and mantle. The only reasonable way to explain the overabundance is by addition of material that is not in equilibrium with the metal core of the Earth (late chondritic veneer).

Introduction:
Metal/silicate partition coefficients are conventionally determined by equilibrating HSE-doped Fe-metal with silicate (e.g., [4],[5]). Recent determinations of one atmosphere metal/silicate partition coefficients of HSEs are based on solubilities of pure HSE-metals in silicate melts. From solubilities metal/silicate partition coefficients are calculated using the activity coefficients of the corresponding HSE in metallic iron. Solubility experiments at one atmosphere have been performed with Pd, Ir, Au, Re ([3],[6],[7],[8]). The formation of tiny Ir-nuggets in the silicate melt is a major problem for the determination of the solubility of Ir ([6],[8]). Such problems do not exist for Pd and Au ([3],[7]). Therefore, high pressure experiments with Pd appeared more promising.

Experimental:
High pressure - high temperature experiments, within a pressure range of 1 to 20 GPa and a temperature range of 1300° to 1500°C were performed in piston cylinder (PC) and multi anvil (MA) devices. $Pd_{90}Fe_{10}$-alloys were equilibrated with an FeO-containing silicate melt close to a composition of komatiitic basalts (SiO_2 49.1 wt.%, CaO 19.2 %, MgO 10.6 %, Al_2O_3 14.1 %, FeO 7.0 %). To avoid contaminations of capsule material with the sample, the metal alloy was used as capsule material. Small pieces of silicate glass were inserted into the metal capsule. Solid metal and liquid silicate coexist during the experiment. At 2 GPa (PC apparatus) a time series was performed to demonstrate that chemical equilibrium between solid metal and liquid silicate has been obtained. All samples were mounted in epoxy, cut through the center of the metal capsule and polished as microprobe sections. Metal contents and major element silicate compositions were determined by electron microprobe. Highly siderophile element concentrations in silicates were analyzed by an UV ArF excimer laser ablation PlasmaQuad PQ-2^{+} ICP-MS at ANU, Canberra. Pd-containing glasses that had been analyzed by neutron activation analysis were used as Pd-standards.

Results:
Pd-solubilities range from 30 ppm at 1 GPa to about 1 ppm at 20 GPa with a clear tendency for lower solubilities at higher pressures. In most cases three individual analyses were made. The scatter of the data was in most cases larger than the statistical error. The reasons are not clear, formation of nuggets cannot be excluded. From the solubilities metal/silicate partition coefficients were calculated assuming an activity coefficient of Pd in the PdFe-alloy of 0.9. Since the activity coefficient of Fe in the $Pd_{90}Fe_{10}$ alloy is rather low, approximately 0.005 [9], the calculated effective oxygen fugacity of the experiments range from IW+3.7 to IW+4.4.

In the Figure measured metal/silicate concentration ratios vs. pressure are plotted. Each symbol represents an individual ICP-MS analysis. The one atmosphere result of [3] for Pd at 1350°C and an fO_2 of 10^{-6} (IW+4) is indicated by the open star.

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The obtained Pd-metal/silicate partition coefficients range from ca. 10^4 at 1 GPa to $6 \cdot 10^6$ at 20 GPa. This is a factor of 10^3 too high to explain the present upper mantle Pd-content by core-mantle equilibrium. This discrepancy is in reality much larger considering the rather oxidizing conditions of the present experiments. Recalculation to oxygen partial pressures appropriate for core formation (IW-2.3) on the assumption that the effective valence of Pd in silicate melts is +1 as derived from 1 atmosphere experiments would increase the resulting metal/silicate partition coefficients by approximately a factor of 30.

Conclusions:

If core-mantle equilibrium was responsible for the HSE-contents of the Earth's mantle one would expect an effective Pd-metal/silicate partition coefficient of about 1000 (core ≈ 4 ppm, mantle ≈ 4 ppb). The one atmosphere partition coefficient (T=1350°C, IW+4) is with $1.6 \cdot 10^7$ four orders of magnitude too high. As seen in the Figure the Pd-metal/silicate partition coefficient appears to increase with increasing pressure, opposite to the trend required for core-mantle equilibrium. We, therefore, believe that these experiments exclude the possibility that the HSE-abundances in the Earth's mantle were established by core-mantle equilibrium. Addition of a late veneer of chondritic material that was never in equilibrium with core-metal provides the best explanation for the HSE abundances in the Earth's mantle.
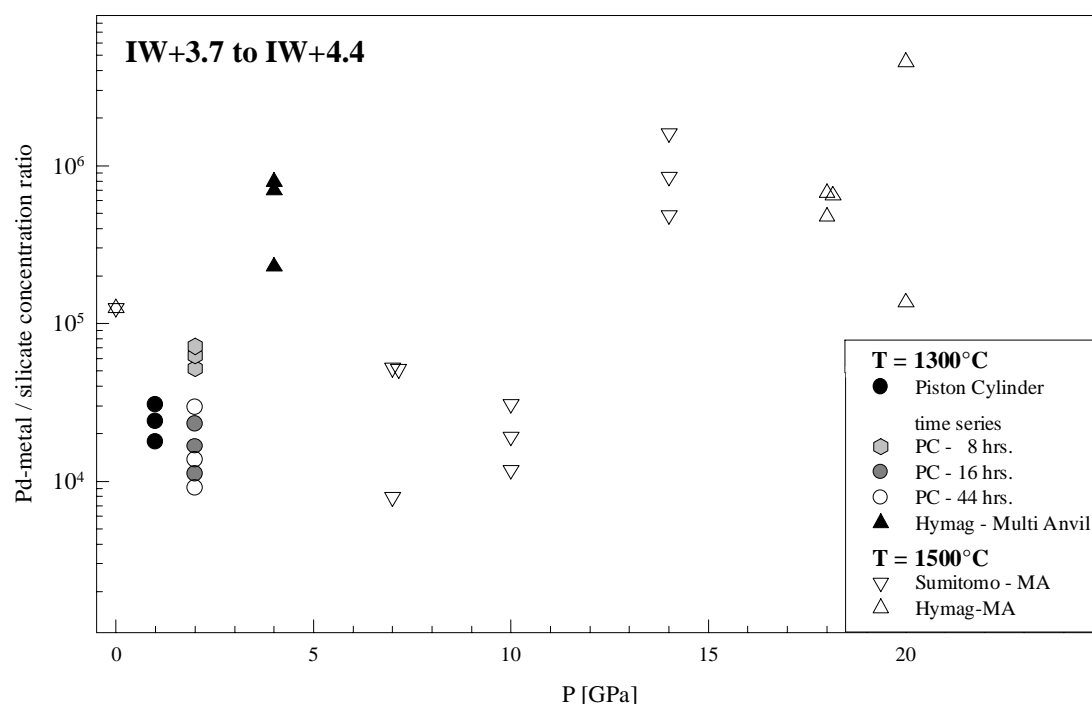
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